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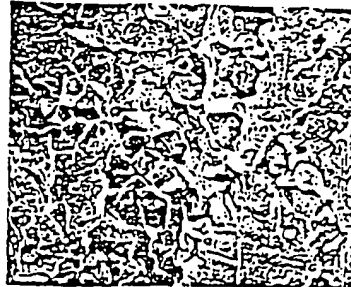
(54) Sintered apatite bodies and composites thereof.

(57) There are provided a novel sintered apatite body and a novel sintered apatite-mineral fiber material composite. The crystals of the sintered apatite have fine dense crystalline structures comprising needle-like fine crystals and are entangled together, whereby the mechanical properties of the sintered apatite body or composite are markedly enhanced. The sintered body and composite wherein the apatite is hydroxyapatite are useful for bioceramic uses. The sintered apatite body or composite is produced by baking under pressure an apatite material alone or in contact with a reinforcing mineral fiber material in the presence of water at a temperature lower than 1000°C, and further at a temperature lower than the temperature causing deterioration of the fiber material in the case of the composite.

FIG. 1



FIG. 2



1

## 5 SINTERED APATITE BODIES AND COMPOSITES THEREOF

10 This invention relates to a sintered apatite body comprising needle-like crystals and a sintered apatite-mineral fiber material composite. More particularly, this invention relates to a process for producing a sintered apatite body and a sintered composite consisting essentially of a matrix amount of an apatite and an effective amount of a reinforcing mineral fiber material, as well as the resulting sintered apatite-mineral fiber material composite. The process for sintering is characterized by baking an apatite material at a defined, relatively-low temperature under pressure in the presence of water.

20 Apatite materials for sintering are typically represented by hydroxyapatite, carbonate-apatite, fluoroapatite and chloroapatite. Processes have been proposed hitherto for sintering these apatites and especially hydroxyapatite by a hot press at high temperatures of about 1100°C or higher in the absence of water. These sintered hydroxyapatite products, however, had a variety of serious problems such as poor mechanical strength properties (especially, impact strength and bending strength) due to their crystalline structures, large pores or flaws, and the like. For example, refer to R.W. RICE et al., J. Am. Ceram. Soc., 63 (3-4), (1980) 129-136, and T. KIJIMA et al., J. Am. Ceram. Soc., 62, (9-10) (1979) 455-460. These sintered apatite products were expected to be useful for broad applications such as ceramic materials, electronic materials, filter materials, bioceramics (e.g., artificial bone and tooth implants) and the like, but it can not be said that they have ever been success-

1 fully utilized in these uses because of their inadequate mechanical properties, etc.

5 Attempts to reinforce sintered apatite with reinforcing materials such as fibers would naturally be considered by those skilled in the art. These attempts, however, have been impeded by the following fundamental problems; (i) sintered apatite bodies baked at such high temperatures are rather brittle and weak in mechanical strength, and thus reinforcement with such fiber materials is not so effective, and (ii) most of such reinforcing materials deteriorate markedly in mechanical strength under the conventional baking conditions of 1100°C or higher for sintering apatite-reinforcing material composites.

15 In accordance with conventional technical ideas for producing a sintered apatite, it has been considered that the satisfactory sintering of a pure apatite material containing no additive compound is substantially impossible at a temperature lower than 1100° or 1000°C and especially lower than 800°C, or that, even when the apatite could be narrowly sintered at such low temperatures, the physical properties of the resulting sintered apatite are inevitably reduced to the point of uselessness. In this connection, the present inventor has surprisingly found that apatite can be sintered under pressurization at a temperature lower than 1000°C and preferably lower than about 800°C in the presence of water to produce a sintered apatite body having far superior mechanical properties and uniform porosity in comparison with conventional sintered apatite.

35 In addition to his intensive investigations into sintered apatite products resulting in the above mentioned invention, the inventor also made intensive investigations into a sintered apatite-reinforcing fiber material

1 composite to further enhance its mechanical properties.  
Initially the present inventor used glass fibers and  
iron fibers which are normally excellent as reinforcing  
materials and readily available at low cost, but the  
5 expected increase in mechanical properties was not  
observed with respect to sintered apatite composites baked  
at about 700°C. The inventor presumed that the problems  
were due to the deterioration of the fiber materials  
under oxidizing atmospheres, even at about 700°C, and  
10 also due to the chemical affinity of the fiber materials  
with apatite at such a temperature. The inventor therefore  
tried to produce apatite-fiber composites wherein glass  
fiber or carbon fiber was used as reinforcing material  
at baking temperatures lower than 400°C and 500°C,  
15 respectively, and unexpectedly succeeded in producing  
apatite composites having excellent properties.

The full reasons for the above-mentioned phenomena have  
not yet been fully clarified. It is conjectured, however,  
20 that glass fiber or iron fiber has physical and chemical  
affinity with apatite at a baking temperature of about  
700°C and thus the reinforcing fiber is deteriorated and  
also firmly bonded to the sintered apatite, whereby a  
sliding action between the fiber and sintered apatite is  
25 lost and the resulting composite is readily broken by a  
force applied thereto. However, the reinforcing fiber  
materials to be used in the present invention have  
sufficient physical affinity with apatite but are complete-  
ly or substantially inert from the viewpoint of chemical  
30 affinity with apatite at a baking temperature of the  
present invention. Thus, it can be conjectured that an  
apatite-reinforcing fiber composite having excellent  
mechanical properties, and especially impact and bending  
strength properties, can be unexpectedly obtained, because  
35 some sliding actions between the fiber material and  
sintered apatite are present in composites according to

1 the present invention. Incidentally, this is rather  
surprising in view of the fact that, in conventional  
resin-fiber composites consisting of fiber materials and  
5 synthetic resins, the bonding affinity between the fibers  
and resins (for example by using a bonding accelerator) is  
desired and taken seriously, but the problems as raised  
above seem different in the case of sintered apatite-mine-  
ral fiber composites because in the case of the resin  
composites the resin itself has some flexibility and the  
10 like. instead of the above mentioned sliding actions.

It is an object of the invention to provide a process  
for producing a novel sintered apatite body and a novel  
sintered apatite-mineral fiber material composite.

15 It is another object of the invention to provide a novel  
sintered apatite body and a novel sintered apatite-  
fiber material composite having broad ranges of applica-  
tions by utilizing their excellent properties.

20 Further objects of the present invention will become  
apparent from the following description.

In accordance with the present invention, there is  
25 provided a process for sintering apatite, which comprises  
baking an apatite material selected from hydroxyapatite,  
carbonate-apatite, fluoroapatite, chloroapatite, precursor  
materials thereof, and mixtures thereof, characterized  
by baking the apatite material in the presence of water  
30 in addition to the crystal water thereof under pressure  
at a temperature lower than 1000°C and preferably lower  
than 800°C to substantially sinter the apatite material.  
Preferably, a matrix amount of the apatite material is  
baked in contact with an effective amount of a reinforcing  
35 mineral fiber material at a temperature lower than 1000°C  
and lower than the temperature causing substantial

1 deterioration of the fiber material.

Further in accordance with the present invention, a  
sintered apatite composite comprising a reinforcing ma-  
5 terial and a sintered apatite matrix wherein the apatite  
is selected from hydroxyapatite, carbonate apatite, fluoro-  
apatite, chloroapatite and mixtures thereof, consists  
essentially of an effective amount of a reinforcing mineral  
fiber material and a matrix amount of sintered apatite  
10 in contact with the fiber material, the crystals of the  
sintered apatite having fine dense crystalline structures  
comprising at least about 30% by weight of needle-like  
fine crystals and are entangled together and the fiber  
material is not substantially deteriorated.

15 Thus, novel sintered apatite bodies are provided having  
fine dense polycrystalline structures wherein the crystals  
comprise or consist essentially of straight and/or curved  
needle-like crystals and are entangled together, which  
20 exhibit excellent physical properties, as well as a  
novel sintered apatite-mineral fiber material composite  
composed of the above mentioned sintered apatite matrix  
and a reinforcing mineral fiber material which is not sub-  
stantially deteriorated and not substantially bonded to  
25 the sintered apatite. The features of the present invention  
are exhibited if at least about 30%, generally 40% or more,  
and preferably about 60% or more by weight, of the sintered  
crystals are composed of the needle-like crystals which  
are entangled together, although normally the crystals  
30 consist essentially of the needle-like crystals.

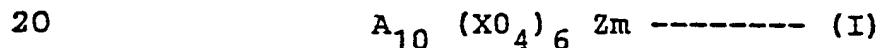
The present invention will be better understood by re-  
ference to the accompanying drawings in which: -

35 Fig. 1 is a scanning electrophotomicrograph  
(magnification x 30,000) of a sintered

1 hydroxyapatite body according to the  
present invention, showing the fine needle-  
like crystalline structures thereof, and

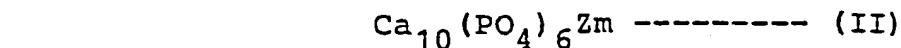
5 Fig. 2 is a scanning electrophotomicrograph  
(magnification x 7,500) of a sintered  
hydroxyapatite body according to a  
conventional sintering process at a high  
10 temperature, showing the hexagonal-system  
crystalline structures thereof.

The apatites used in the present invention include,  
hydroxyapatite, carbonate-apatite, fluoroapatite, chloro-  
apatite, mixtures thereof, and mixtures of subunit  
15 materials thereof which are converted to these apatites in  
the course of the baking step hereinafter referred to as  
an apatite precursor). Apatite compounds are broadly defi-  
ned by the following formula (I);



wherein, A = Ca, Pb, Mn, Na, K, etc.; X = P, As, V, Si,  
etc.; Z = OH, CO<sub>3</sub>, F, Cl; and m is a number to satisfy the  
atomic valences. The apatite to be used in the present  
25 invention, however, is more limited.

The apatites used in the present invention are  
those compounds which have fundamental structures repre-  
sented by the following formula (II) and of which the  
30 atomic ratio of calcium to phosphorus (hereinafter  
referred to as Ca/P ratio) is within the range specified  
below;



wherein, Z is selected from OH, CO<sub>3</sub>, F, Cl and mixtures

1 thereof, and  $m$  is a number satisfying atomic valences  
substantially (e.g., 2 or 1). More specifically, in the  
formula (II) given above, the Ca/P ratio is not necessari-  
ly a stoichiometric ratio (5/3) but can be a non-stoichio-  
5 metric ratio. In general, the Ca/P ratio is approximately  
in the range of 4/3 to 11/6 and preferably about 9/6 to  
about 5/3. If required an inorganic non-phosphorus calcium  
compound such as calcium hydroxide can be intimately  
mixed with an apatite material having a Ca/P ratio of less  
10 than 5/3 to adjust its Ca/P ratio to about 5/3. In the  
case where a carbonate group-containing calcium compound  
such as calcium carbonate is used therefor, a sintered  
apatite body or apatite-fiber composite containing  $\text{CO}_3$   
groups can be obtained by baking the materials at a tem-  
15 perature lower than the decomposition temperature of the  
carbonate compound. It is to be noted that, in the  
apatite represented by the formula (II), the Ca and/or  
P atom may be substituted by a small or impure amount of  
other atoms as illustrated in the definition of formula  
20 (I).

The symbol  $Z$  in formula (II) above can be one or two or  
more atoms or groups selected from OH,  $\text{CO}_3$ , F and Cl.  
In this case, the apatite is herein classified into hydro-  
25 xy-apatite, carbonate-apatite, fluoroapatite or chloro-  
apatite, respectively, in accordance with the largest  
amount of OH,  $\text{CO}_3$ , F or Cl contained therein. All these  
apatites fall within the same hexagonal crystalline  
system, space group  $\text{C6}_3/\text{m}$ , and chemical formula number  
30 in unit lattice, and thus they have substantially the  
same sintering properties and similar physical properties.  
These apatites are available commercially and can be  
purified as necessary, or can be synthesized chemically.

35 From the viewpoint of uses and the like, the apatite to  
be used in the present invention is preferably hydroxy-



- 1 apatite represented by the formula (II) above wherein  
substantially all or a major amount (normally about 90%  
or more) of Z is OH group and the balance amount (normally  
about 10% or less) of Z if any is the other substituents.  
5 For bioceramic uses, the balance of Z if any is preferred  
to be substantially CO<sub>3</sub> group.

By the term "a matrix amount" of apatite used with respect  
to the apatite-fiber material composite is meant the  
10 amount of the apatite material which can bind a reinfor-  
cing mineral fiber material (hereinafter sometimes re-  
ferred to as fiber material) by the sintered apatite to  
form the sintered composite. The term "an effective amount"  
of the fiber material means the amount thereof which can  
15 reinforce the sintered composite and can be bound by the  
sintered apatite matrix to form the sintered composite.

Although the effective amount of the fiber material  
depends on the density and the like of the fiber material  
20 to be used, the ratio of the effective amount of fiber  
materials to the matrix amount of apatites is by weight  
preferably in the range of 0.5-70% to 99.5-30%, desirably  
1-50% to 99-50%, preferably 2-40% to 98-60%, more preferab-  
ly 5-30% to 95-70%, and typically 7-25% to 93-75%.

25 Consequently, the actual amount of the fiber material is  
in the range of about 1% to about 50% by weight, and the  
amount of the apatite material is in the range of about  
99% to about 50% by weight.

30 The sintered composite of the present invention can, of  
course, also contain optional materials such as fillers  
and coloring agents which are compatible with the apatite  
and fiber materials and are inert under the conditions  
35 of baking, machining and uses, so far as the properties  
of the resulting composite are not substantially deteriora-  
ted.

1 The mineral fiber materials to be used essentially as  
reinforcing materials encompass mineral (i.e. inorganic  
or metallic) fiber materials which have sufficient strength  
and will not be substantially deteriorated when they are  
5 baked in contact with the apatite material in the presence  
of moisture for at least 0.5 hour at a sintering tempera-  
ture higher than about 150°C and preferably above 170°C  
(but lower than 1000°C or 800°C). The fiber materials  
preferred for use in the present invention preferably  
10 include, for example, mullite fibers (800°C), nitrogen-  
modified mullite (Sialon) fibers (1000°C), silicon carbide  
fibers (800°C), carbon fibers (500°C), apatite glass  
fibers (750°C), glass fibers and alkali-resistant glass  
fibers (500°C), as well as silicon nitride fibers (1000°C),  
15 silica fibers (1000°C), alumina fibers (1000°C), and the  
like, the temperatures shown in the parentheses being the  
approximate maximum values at which the fiber-containing  
apatite composite material can be baked according to the  
present invention without deteriorating the properties  
20 of the fiber material or the sintered apatite. Moreover,  
chemically inert metallic fiber materials such as metallic  
fibers coated thereon with an inorganic element or compound  
or substantially inert metallic fibers can also be used  
as the reinforcing fiber materials. Coated metallic fibers  
25 are generally preferred. For example, boron fibers wherein  
boron was vapor-deposited onto tungsten fibers can be  
advantageously used.

These reinforcing fiber materials are not restricted to  
30 the materials illustrated above and can be used alone or  
as optional mixtures thereof, as far as they exhibit  
satisfactory reinforcing effects and are not deteriorated  
in the course of baking. As to the forms and dimensions  
of the reinforcing fiber materials, technical knowledge  
35 of conventional glass fiber-synthetic resin composites  
can be applied. For example, they can be in the form of

1 short fibers, long fibers, fiber yarns, fiber strands,  
wooly fibers, whiskers, nonwoven or woven fabrics, mixtures  
thereof, and the like. In the case of short fibers, the  
5 fiber length thereof is desirably longer than the crystal  
length of the sintered apatite. The distribution of the  
mineral fiber material in the present sintered apatite com-  
posite can be in a state substantially orientated mono-,  
bi- or triaxially or in a state substantially unorientated  
and distributed irregularly. Also, the distribution of the  
10 fiber material can be uniformly dispersed in the sintered  
apatite matrix or dispersed variably, dense (or rare or  
zero) toward the core of the composite and rare or zero  
(or dense) toward the surfaces of the composite. It is  
preferred that the fiber material is distributed dense  
15 toward the surface and is not exposed to the surface from  
the viewpoint of stress-resistant structural materials.

The sintered apatite body of the present invention can  
be produced by baking the above mentioned apatite material  
20 under pressure in the presence of a suitable amount of  
water at a temperature of about 150°C to less than 1000°C  
and preferably about 160°C to about 800°C. When the  
sintering temperature is lower, the needle-like crystalline  
structures peculiar to the present sintered apatite tend  
25 to become finer and increase in mechanical strength. This  
tendency is markedly noted when the sintering temperature  
is normally about 700°C or less, especially about 600°C  
or less and typically about 500°C or less, although the  
sintering is accelerated at a higher temperature. Thus,  
30 the lower sintering temperature is generally preferred  
in the present invention from the viewpoint of the  
enhanced mechanical properties of the resulting sintered  
body or composite. Usually, the amount of water to be co-  
existing with the apatite material in the baking step  
35 is in addition to crystal water, an amount of non-crystal  
water (i.e. water except crystal water) in the range of

1 0.01% to about 25%, preferably about 0.05% to about 20%,  
more preferably about 0.1% to about 20% and typically  
about 3% to about 18% by weight of the apatite material  
used. When the amount of water is large, the sintering  
5 of the apatite tends to be accelerated. In the case where  
the water is more than about 25% and pressure is  
relatively low, the voids of the resulting sintered apatite  
will generally become too large. However, when the  
apatite is baked in an open-heating means such as a hot  
10 press, the amount of water to be charged may be larger  
than 25%.

In the same fashion and conditions as described above,  
the mineral fiber-sintered apatite composite of the  
15 present invention can be produced by baking a matrix  
amount of the apatite material and an effective amount  
of the reinforcing mineral fiber material in a substan-  
tially contacted state at a temperature defined above  
and lower than the temperature causing substantial  
20 deterioration of the fiber material and substantial  
bonding thereof to the apatite material.

Although the sintering mechanism of the apatite in the  
present invention has not yet been fully clarified, it  
25 is assumed that the apatite is dissolved and separated  
out at the baking temperature and then the separated  
apatite is recrystallized, entangled together and sintered.  
The dissolution and separation of apatite tend to be pro-  
moted under a higher pressure and/or in the presence of  
30 sufficient water. In this connection, in accordance with  
the present invention, the baking or sintering temperature  
can be considerably lowered under a higher pressure and  
in the presence of sufficient water in the baking step.  
Thus, the pressure to be employed in the sintering of the  
35 present invention is at least about 5 kgf/cm<sup>2</sup>, preferably  
about 50 kgf/cm<sup>2</sup> or more, and typically about 500 kgf/cm<sup>2</sup>  
or more.

1 In the baking step of the present invention, conventional  
techniques known to the sintering art can be employed.  
For example, a hot press method under a steam atmosphere  
can be used, or a closed heating method under pressure  
5 by means of an autoclave and the like, a closed high-  
frequency heating method under pressure, a hot isotactic  
pressing method, etc. The typical methods for the baking  
are summarized in the following. The time of baking is  
generally in the range of about 0.5 to about 30 hours.

10

(i) Hot press method

The material such as an apatite material, a mixture of  
an apatite material and a mineral fiber material, or a  
premolded article thereof may be baked at a temperature  
15 defined above by means of a hot press under a pressure  
of about 5 kgf/cm<sup>2</sup> or more by applying thereto an atmosphere  
of steam or a steam-containing inert gas, preferably at  
a temperature of about 150°C to about 500°C under a pressure  
of about 10 to about 1000 kgf/cm<sup>2</sup>. This method, however,  
20 may be rather difficult to give constant sintering condi-  
tions.

(ii) Closed heating method under pressure

The material as mentioned above may be baked in the  
25 presence of water at a temperature defined above by means  
of a pressure-proof vessel such as an autoclave under a  
pressure of five to several thousands atmospheres. When  
both the temperature and pressure are relatively low, a  
relatively longer time is needed for sintering the ma-  
30 terial. When the pressure is as high as 1000 kgf/cm<sup>2</sup> or  
more, the sintering can be advantageously conducted even  
at a temperature of 150°C to about 200°C. Preferably, the  
material can be baked at a temperature of about 150°C to  
about 500°C under a pressure of about 20 to about 2000  
35 kgf/cm<sup>2</sup>.

- 1 (iii) Sintering in a sealed pressure-deformable capsule,  
etc.

In the closed heating method, closed high-frequency heating method, hot isotactic pressing method and the  
5 like described above, the material mentioned above can be sintered more effectively by baking the material which has been sealed in a pressure-deformable chemically-inert vessel (e.g., a capsule or a tube) together with water. The baking conditions are substantially the same as in  
10 (ii) above, and preferably at a pressure of about 40 to about 3000 kgf/cm<sup>2</sup> and a temperature of about 150°C to about 500°C. By employing such a sealed vessel, the contents of the material and water can be maintained unchanged.

- 15 Of the methods described above, method (ii) is preferred and method (iii) is most preferred. An apatite material or a mixture of an apatite material and a reinforcing fiber material can be molded into a desired shape by means of pressing or the like before the baking step;  
20 or the resulting sintered apatite body or composite can be machined into a desired shape.

The sintered apatite body obtained according to the present invention comprises or consists essentially of fine  
25 dense polycrystalline structures wherein the crystals are needle-like fine crystals and are entangled together, and the sintered apatite can be provided with suitable microporosity as necessary. The sintered apatite-fiber material composite is a composite wherein the fiber material is  
30 present in the unchanged state in contact with the sintered apatite matrix having the above mentioned crystalline structures, and the sintered composite can also be provided with suitable microporosity. In accordance with the sintering conditions of the present invention, the crystals  
35 of the present sintered apatite body or matrix have fine dense polycrystalline structures wherein the crystals

1 comprise or consist essentially of straight and/or curved  
needle-like fine crystals and are entangled together,  
whereby the mechanical strength properties of the present  
sintered apatite body or apatite-fiber material composite  
5 are enhanced markedly. According to the conventional process for sintering the apatite at a temperature as high as 1100°C, the resulting sintered apatite is composed of relatively large hexagonal system crystals, and thus has markedly decreased mechanical strength properties.

10 The strength properties of the sintered apatite body or composite is naturally reduced when the void volume or pore size of the sintered apatite body or matrix is too large. In order to obtain a sintered apatite body or  
15 composite having both excellent strength and sufficient microporosity, it is desired that the sintering process is carried out under a relatively high pressure at a temperature as low as possible in the presence of moisture. The micropores obtained according to the present invention  
20 are normally in the form of open (continuous) pores.

The properties of the sintered apatite body and the sintered apatite-fiber material composite according to the present invention can have, for example, the following  
25 approximate values.

(a) Mean diameter of sintered apatite crystals:

0.01 to 5  $\mu\text{m}$   $\phi$

(b) Mean length of sintered apatite crystals:

1 to 1000  $\mu\text{m}$

(c) Mean pore size of sintered apatite:

5 to 1000  $\mu\text{m}$

(d) Voids of sintered apatite:

0 to 60% by volume

(e) Compression strength of sintered apatite:

300 to 1500  $\text{kgf/cm}^2$

- 1 (f) Bending strength of sintered apatite:  
100 to 800 kgf/cm<sup>2</sup>
- (g) Impact strength of sintered apatite:  
10 to 40 kgf.cm/cm<sup>2</sup>
- 5 (h) Tensile strength of sintered apatite:  
40 to 70 kgf/cm<sup>2</sup>
- (i) Compression strength of sintered composite:  
350 to 2000 kgf/cm<sup>2</sup>
- (j) Bending strength of sintered composite:  
10 1000 to 3500 kgf/cm<sup>2</sup>
- (k) Impact strength (charpy) of sintered composite:  
50 to 200 kgf.cm/cm<sup>2</sup>
- (l) Tensile strength of sintered composite:  
70 to 350 kgf/cm<sup>2</sup>

15

Some typical properties of conventional sintered apatite bodies and composites, which were sintered at about 1100°C by means of a hot press without a steam atmosphere applied thereto, are shown in Comparative Examples I to III below.

20

The sintered apatite body and apatite-fiber composite can be advantageously applied in a broad range of uses and especially in fields where strength properties are required. Typical applications are ceramic materials which need strength properties, electronics materials, filter materials, chromatographic carriers, sensor elements (especially for physiological use), bioceramics (e.g. artificial bone, tooth and joint for the human or animal bodies), other uses where conventional fine ceramics are utilized, and the like. The above mentioned applications can be classified into industrial ceramic materials and bioceramic materials. The bioceramics require compatibility with living organisms such as the human or animal bodies in addition to strength properties and microporosity. This compatibility will be discussed in the following.

25

30

35



1 It is known that hard tissues (bone, tooth, etc.) of  
mammals and especially human bodies consist essentially  
of densified hydroxyapatite and more specifically consist  
5 of densified hydroxyapatite containing a small amount  
(several %) of  $\text{CO}_3$  group. In this connection, much  
research has been reported on using sintered hydroxy-  
apatite bodies for artificial bone and tooth implants.  
For example, refer to M. JARCO et al., J. Bioeng., 1,  
(1977) 79 and E.B. NERY et al., J. Periodontol, 46, (1975)  
10 328. Especially, porous sintered hydroxyapatite having  
a void of several percent or more has been appreciated  
to be practically satisfactory for compatibility with  
human tissues. Conventional sintered hydroxyapatite, how-  
ever, is not used in practice at present, which may be  
15 essentially due to non-uniform porosity and unsatisfactory  
mechanical properties such as impact strength and bending  
strength. On the other hand, mineral fiber materials to  
be used in the present invention and especially fiber  
materials of carbon, silicon carbide, mullite, nitrogen-  
20 modified mullite (Sialon), silica, alumina, apatite glass  
and silicon nitride are known to have chemically and  
physiologically non-irritating properties as well as  
excellent strength and elasticity. Moreover, it has been  
appreciated in the art that these fiber materials are in  
25 practice satisfactory for compatibility with human  
tissues. These fiber materials are satisfactory for the  
physiological compatibility especially when they are in-  
cluded as the composite in the sintered hydroxyapatite  
matrix. It is generally preferred that the surface of the  
30 present composite for bioceramic uses is substantially  
covered with the apatite matrix, that is, the fiber  
material is not substantially exposed.

The preferred strength properties and open micropores  
35 having a void of 3% to about 60% and normally 5% to 50%  
by volume which have been required for such bioceramics

-17-

1 are sufficiently provided by the sintered hydroxyapatite  
body and composite according to the present invention.  
Thus, artificial hard tissue materials having suitable  
open pores, satisfactory strength properties and compati-  
5 bility with human and animal bodies can be obtained accor-  
ding to the present invention, wherein the above described  
conventional problems have been eliminated. In other words,  
because it has been confirmed in the art that conventional  
porous sintered hydroxyapatite bodies have compatibility  
10 with human tissues as shown in the above mentioned litera-  
ture, the present sintered hydroxyapatite body and  
composite thereof improved in mechanical properties,  
suitable open pores, etc. can be used satisfactorily as  
such bioceramics.

15 Again, the mode how the sintered hydroxyapatite body is  
successfully united with human (or animal) tissues has not  
yet been fully elucidated. It is believed, however, that,  
when a hydroxyapatite bioceramic material such as tooth  
20 or bone substitute is implanted in human tissues, the  
human body fluids such as blood contact the bioceramic  
material and pass through the open micropores of the bio-  
ceramic material without rejection symptoms, and thus the  
hydroxyapatite components contained in the body fluids  
25 gradually deposit onto the micropores and surface of the  
hydroxyapatite bioceramic material to form natural  
deposition-densified hydroxyapatite layers, whereby the  
sintered hydroxyapatite body can be successfully unified  
with the human tissues by the aid of the natural densified  
30 hydroxyapatite layers. In the case of the present sintered  
hydroxyapatite-reinforcing mineral fiber material composite,  
the same mode of unification with human tissues can be  
applied because the fiber material is substantially covered  
with or is contained in the sintered hydroxyapatite matrix  
35 and also the fiber material itself is compatible with  
human tissues. In this connection, it is preferred that

1 hydroxyapatite bioceramic materials have a Ca/P ratio in the vicinity of its theoretical value 5/3, e.g., in the range of about 9/6 to about 5/3.

5 The present invention will be further explained by way of the following examples. All the apatite materials to be used in the present invention have substantially the same chemical structures, crystalline systems, sintering properties and the like. Thus, those skilled in the art  
10 can readily produce substantially the same or similar sintered apatite bodies or composites of the present invention on the basis of the disclosure herein by using the materials and/or processes other than those shown in the Examples.

15

In the following examples, the ratios and percentages are by weight unless otherwise specified.

#### Example 1

20 Hydroxyapatite containing hydroxyl group and no other atom or group as the substituent (Ca/P ratio = 95/60) was adjusted to a water content (except crystal water) of 5%. The hydroxyapatite powder was sealed in a pressure-deformable silver tube and then baked at 500°C under a  
25 pressure of 1000 kgf/cm<sup>2</sup> for 3 hours by means of a pressure-tight vessel. The resulting sintered apatite body exhibited the following properties.

30	Compression strength	520 kgf/cm <sup>2</sup>
	Bending strength	710 kgf/cm <sup>2</sup>
	Tensile strength	55kgf/cm <sup>2</sup>
	Impact strength (Charpy)	16 kgf.cm/cm <sup>2</sup>
	Voids (open micropores)	about 24% by volume

35 The crystals of the sintered body are shown in Fig. 1 (magnification x 30,000) wherein fine needle-like crystals are entangled together.

1 Example 2

A mixture of 85% hydroapatite powder used in Example 1 and 15% carbon fiber having a mean length of about 9 mm (thermal decomposition process grade) was adjusted to a water content of 5%. The mixture was then sealed in a pressure-deformable silver tube and baked at 400°C for 7 hours as in Example 1. The resulting sintered apatite composite exhibited the following properties, the units of the strength properties being the same as in Example 1.

Compression strength	780
Bending strength	1850
Tensile strength	200
Impact strength (Charpy)	115

15 It was observed in the bending test that on the rupture cross-section the carbon fibers were somewhat drawn out of the cross-section surface and ruptured. This demonstrates that some sliding actions exist between the fiber material and sintered apatite in the resulting composite.

20 Example 3

The process of Example 2 was repeated except that 15% of mullite fiber having a mean length of about 9 mm was used instead of the carbon fiber. The resulting sintered apatite composite exhibited the following properties, the units of the strength properties being the same as in Example 1.

30 Compression strength	690
Bending strength	1720
Tensile strength	185
Impact strength (Charpy)	110

35 It was again observed in the bending test that the mullite fibers were somewhat drawn out of the rupture cross-section and ruptured.

1 Example 4

Calcium carbonate powder was incorporated into the hydroxyapatite powder (Ca/P ratio = 95/60) to make the Ca/P ratio of the resulting mixture about 99/60. The mixed powder 85% was admixed with 15% of carbon fiber having a mean length of about 9 mm (thermal decomposition process grade). The resulting mixed material was adjusted to a water content of 5%, sealed in a pressure-deformable silver tube, and baked as in Example 2. The resulting sintered apatite composite exhibited the following properties, the units being the same as in Example 1. Incidentally, it is especially preferred from the viewpoint of compatibility with human tissues that the resulting composite contains a suitable amount of CO<sub>3</sub> group.

15

Compression strength	820
Bending strength	1870
Tensile strength	195

20 Example 5

The process of Example 4 was repeated except that the carbon fiber and calcium carbonate were replaced by 15% of silicon carbide fiber having a mean length of about 9 mm and by the corresponding amount of calcium hydroxide powder to make the Ca/P about 99/60, respectively. The resulting sintered apatite composite exhibited the following properties, the units being the same as in Example 1.

25

Compression strength	835
Bending strength	1910
Tensile strength	190

30

Comparative Example I

Hydroxyapatite containing hydroxyl group and no other atom or group as the substituent (Ca/P ratio = 95/60) was molded into a tablet about 5 mm x about 50 mm Ø and then

35

1 adjusted to a water content of 5%. The hydroxyapatite  
was compressed and baked at 1100°C under 200 kgf/cm<sup>2</sup> for  
2 hours by means of a hot press. The resulting sintered  
apatite body of the conventional type exhibited the  
5 following properties, the units being the same as in  
Example 1.

	Compression strength	320
	Bending strength	310
10	Tensile strength	35
	Impact strength (Charpy)	7

The crystals of the resulting sintered body are shown  
in Fig. 2 (magnification x 7,500), which are composed of  
15 hexagonal system crystalline structures.

#### Comparative Example II

A mixture of 85% hydroxyapatite powder used in Comp.Ex.I  
and 15% carbon fiber having a mean length of about 9 mm  
20 (thermal decomposition process grade) was molded into  
a tablet and then adjusted to a water content of 5%.  
The tablet was sintered as in Comp.Example I to show the  
following properties, the units being the same as in  
Example 1.

25

	Compression strength	310
	Bending strength	320
	Tensile strength	40
	Impact strength (Charpy)	8

30

#### Comparative Example III

The process of the above Comp.Ex. II was repeated except  
that 15% of glass fiber having a mean length of about 9 mm  
was used instead of the carbon fiber. The resulting  
35 sintered apatite composite exhibited the following proper-  
ties, the units being the same as in Example 1.

-22-

1	Compression strength	305
	Bending strength	310
	Tensile strength	45
	Impact strength	8

5

Indicentally, in Comparative Examples II and III, it was observed in the bending test that the carbon fibers or glass fibers were ruptured on the cross-sectional surfaces. These facts demonstrate that the fiber materials were deteriorated and also firmly bonded to the sintered apatite in the resulting composites. Also, it is to be noted that the hot press sintering steps in Comparative Examples I to III were conducted without applying a steam atmosphere thereto. This sintering step corresponds to the baking of hydroxyapatite in the absence of water, since substantially all the water present in the apatite is rapidly vaporized away from the mold of the hot press.

10

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#### Example 6

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The process of Example 2 was repeated except that 95% of the hydroxyapatite powder and 5% of carbon fiber were used. The resulting sintered apatite composite exhibited compression strength of 660 kgf/cm<sup>2</sup>.

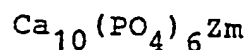
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1. CLAIMS:

1. A process for sintering apatite by baking an apatite material selected from hydroxyapatite, carbonate apatite, fluoroapatite, chloroapatite, precursor materials thereof, and mixtures thereof; characterized by baking the apatite material in the presence of water in addition to the crystal water thereof under pressure at a temperature lower than 1000°C to substantially sinter the apatite material.
2. A process according to Claim 1, in which a matrix amount of the apatite material is baked in contact with an effective amount of a reinforcing mineral fiber material at a temperature lower than 1000°C and lower than the temperature causing substantial deterioration of the fiber material.
3. A process according to Claim 1 or 2, in which the crystals of the sintered apatite have fine dense crystalline structures wherein the crystallites contain at least 30% by weight of needle-like fine crystals and are entangled together.
4. A process according to any one of Claims 1 to 3, in which the apatite has the fundamental structure represented by the following formula and the atomic ratio of calcium to phosphorus in the apatite is in the range of 4/3 to 11/6;



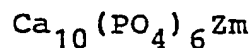
wherein, Z is selected from OH, CO<sub>3</sub>, F, Cl and mixtures thereof and m is a number satisfying atomic valences.



1 5. A process according to any one of Claims 1 to 4,  
in which a small amount of an inorganic non-phosphorus  
calcium compound is intimately mixed with an apatite  
material having a calcium/phosphorus ratio of less than  
5 5/3 to adjust the Ca/P ratio of the apatite material to  
about 5/3.

6. A sintered apatite composite comprising a rein-  
forcing material and a sintered apatite matrix wherein  
10 the apatite is selected from hydroxyapatite, carbonate  
apatite, fluoroapatite, chloroapatite and mixtures  
thereof, consisting essentially of an effective amount  
of a reinforcing mineral fiber material and a matrix  
amount of sintered apatite in contact with the fiber  
15 material, the crystals of the sintered apatite having  
fine dense crystalline structures comprising at least  
about 30% by weight of needle-like fine crystals and are  
entangled together, and the fiber material is not sub-  
stantially deteriorated.

20 7. A composite according to Claim 6, in which the  
apatite has the fundamental structure represented by the  
following formula and the atomic ratio of calcium to  
phosphorus in the apatite is in the range of 4/3 to  
25 11/6;



wherein, Z is selected from OH, CO<sub>3</sub>, F, Cl and mixtures  
30 thereof and m is a number satisfying atomic valences.

8. A composite according to Claim 6 or 7, in which  
the amount of the fiber material is in the range of  
about 1% to about 50% by weight and the amount of the  
35 apatite material is in the range of about 99% to about  
50% by weight.

11 11 11

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1 9. A composite according to any one of Claims 6 to  
8, in which the sintered apatite has open pore voids of  
3% to 60% by volume, preferably of 5% to 50% by volume.

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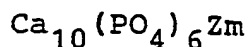
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## 1 CLAIMS:

1. A process for sintering apatite by baking an apatite material selected from hydroxyapatite, carbonate apatite, fluoroapatite, chloroapatite, precursor materials thereof, and mixtures thereof; characterized by baking the apatite material in the presence of water in addition to the crystal water thereof under pressure at a temperature lower than 1000°C to substantially sinter the apatite material.
2. A process according to Claim 1, in which a matrix amount of the apatite material is baked in contact with an effective amount of a reinforcing mineral fiber material at a temperature lower than 1000°C and lower than the temperature causing substantial deterioration of the fiber material.
3. A process according to Claim 1 or 2, in which the crystals of the sintered apatite have fine dense crystalline structures wherein the crystallites contain at least 30% by weight of needle-like fine crystals and are entangled together.
4. A process according to any one of Claims 1 to 3, in which the apatite has the fundamental structure represented by the following formula and the atomic ratio of calcium to phosphorus in the apatite is in the range of 4/3 to 11/6;

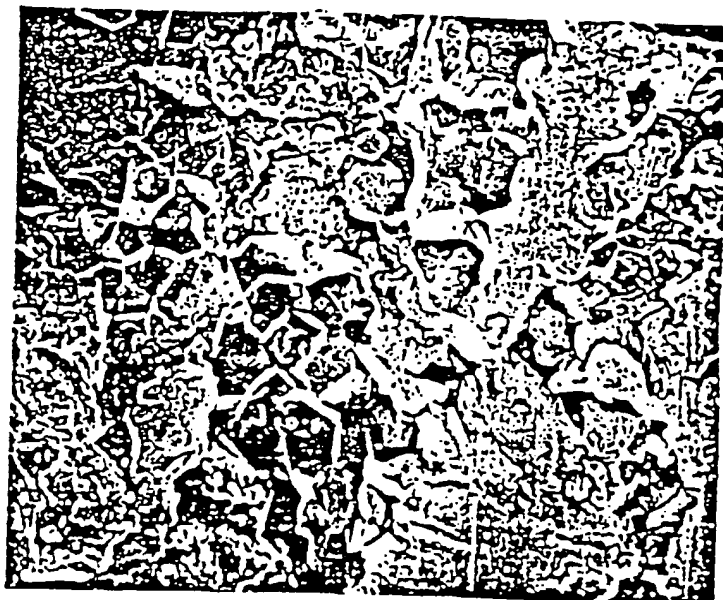


wherein, Z is selected from OH, CO<sub>3</sub>, F, Cl and mixtures thereof and m is a number satisfying atomic valences.

FIG. 1



FIG. 2



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 C 04 B 35/00, C 04 B 35/80  
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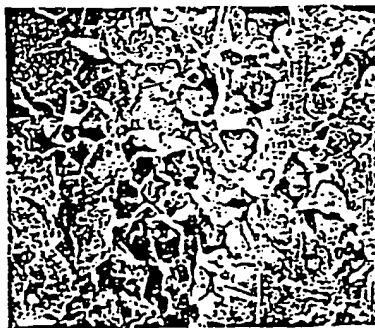
54 Sintered apatite bodies and composites thereof.

57 There are provided a novel sintered apatite body and a novel sintered apatite-mineral fiber material composite. The crystals of the sintered apatite have fine dense crystalline structures comprising needle-like fine crystals and are entangled together, whereby the mechanical properties of the sintered apatite body or composite are markedly enhanced. The sintered body and composite wherein the apatite is hydroxyapatite are useful for bioceramic uses. The sintered apatite body or composite is produced by baking under pressure an apatite material alone or in contact with a reinforcing mineral fiber material in the presence of water at a temperature lower than 1000°C, and further at a temperature lower than the temperature causing deterioration of the fiber material in the case of the composite.

FIG. 1



FIG. 2





European Patent  
Office

# EUROPEAN SEARCH REPORT

**104640**  
Application number

EP 83 10 9582

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	CHEMICAL ABSTRACTS, vol. 94, no. 22, June 1981, page 296, no. 179537w, Columbus, Ohio, US; & JP - A - 80 130 854 (MITSUBISHI MINING AND CEMENT CO., LTD.) 11-10-1980 * abstract *	1,3,4	C 04 B 35/64 C 04 B 35/00 C 04 B 35/80 A 61 F 1/00 //
A	IDEM	6,7,9	
X	--- GB-A-1 550 330 (ASAHI KOGAKU KOGYO K.K.) * claims 1-5; page 1, lines 62-71, 77-82; page 2, lines 1-48 *	1-4,6-9	
A	--- JOURNAL OF CRYSTAL GROWTH, vol. 46, 1979, pages 213-220, North-Holland Publishing Co., Amsterdam, NL; J. ARENDS et al.: "Preparation of pure hydroxyapatite single crystals by hydrothermal recrystallization" * pages 213-214, paragraph 2.1; pages 214-215, paragraphs 2.3; pages 218-219, figure 7 and paragraph 4 *	1,3-7	TECHNICAL FIELDS SEARCHED (Int. Cl. 3)  C 04 B A 61 F
A	--- US-A-4 149 894 (M. EBIHARA) * claim 1; column 2, lines 29-34 *	1-7,9	
---		-/-	
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>19-12-1984</b>	Examiner <b>SCHURMANS H.D.R.</b>
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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
A	EP-A-0 026 090 (KUREHA KAGAKU KOGYO K.K.) * claims 1,5-7; page 6, lines 13-36; page 10, lines 2-34; page 11, lines 14-20 *	1-7,9	
A	GB-A-1 487 181 (COLGATE-PALMOLIVE CO.) * claim 1; page 2, lines 111-125 *	1-7,9	
P,X	CHEMICAL ABSTRACTS, vol. 98, no. 4, January 1983, page 259, no. 21088y, Columbus, Ohio, US; K. HIROTA et al.: "Densification of hydroxylapatite by hot isostatic pressing" & YOGYO KYOKAISHI 1982, 90(11), 680-2	1,3,4,5	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19-12-1984	Examiner SCHURMANS H.D.R.
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